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## (54) Aqueous composition.

(57) An aqueous composition is described. The composition comprises a film-forming latex polymer having anionic character; a water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups; and a volatile base in an amount effective to raise the pH of the composition to a point high enough where essentially all of the amine functional groups are in a nonionic state; and optionally a water-soluble or water-dispersible multivalent metal. The composition provides an aqueous, quick-set noncementitious composition which is easily applied, develops early cohesive strength and leaves no waste under all curing conditions. The invention is particularly useful as an adhesive used in exterior insulating and finishing systems. The composition also provides an aqueous, exterior, quick-set coating composition having early washout resistance and dirt pick-up resistance. The invention is also particularly useful as a binder used in a traffic paint and as a base coat and/or top coat in exterior insulation finishing systems.

EP 0 594 321 A1

Th present inv ntion r lates to an aqueous composition. In particular, the present inv ntion relates to an aqu ous, quick-set, non-cementitious adhesiv . Mor in particular, the present inventi n relates t an aqueous, quick-set, non-cementitious adhesive which provid s arly cohesive and adh siv strength and to a method for improving the early cohesive and adh sive strength of non-c mentitious adhesiv s. Also, in particular, the present inv ntion relat s to improved quick-s t xterior coatings. Also, mor in particular, th present invention relates to aqueous, exterior quick-set coatings which are storage stabl , provid early washout and dirt pick-up resistance and long term durability and to a method for improving the early washout and dirt pick-up resistance of aqueous, exterior quick-set coatings.

Exterior insulation and finishing systems ("EIFS") are multilayered composite systems installed on the outsides of buildings and other outdoor structures to insulate, protect and beautify. The exterior surface of the building or other outdoor structure may be constructed of concrete, cinder block, stone, brick, wood, gypsum board and the like. A layer of material, typically in the form of a solid or foamed sheet of material such as for example foamed and extruded polystyrene, is applied to the exterior surface of the building or other outdoor structure and is covered with a mesh-reinforced basecoat and then a topcoat.

The basecoat provides weather resistance, flexibility, toughness, mechanical strength and impact strength to the system. The topcoat provides aesthetic features to the surface of the system, such as for example color and texture.

If a mechanical fastening means is not used, an adhesive is needed to bond the layer of material to the exterior surface of the building or other outdoor structure. The adhesive may or may not contain cement. Problems are encountered both with adhesives which contain cement and adhesives which do not contain cement.

Calcium oxide, silica, alumina and iron oxide, in appropriate proportions, chemically combine at high temperatures to form a composite of hydraulic cement. When the hydraulic cement is contacted with water, its constituents begin to hydrate and to set into a hard substance typically on the order of one to three hours. This leaves only a short pot life for the application of adhesives which contain cement while they are still fluid. Contractors using a cement-containing adhesive must discard any unused material because it will not be usable after setting into a hard substance, usually in less than about five hours. This leads to considerable waste.

This waste problem may be avoided by using non-cementitious adhesives. However, conventional non-cementitious adhesives have experienced poor early adhesive and early cohesive problems because they lack the adhesive and cohesive strength provided by the cement. This drying time may be several days depending upon the environmental conditions. The problem is further exacerbated because the layer of material applied to the exterior surface of a building or other outdoor structure is typically a hydrophobic material, such as polystyrene foam, which impedes the movement of water out of the layered exterior finishing system. Until the layered exterior finishing system sets, the adhesive does not have sufficient cohesive and adhesive strength to bond the layer of material to the exterior surface of a building or other outdoor structure. This is particularly a problem in areas where the materials might be disturbed or where the weather is cold and wet or humid.

Contractors typically install EIFS in layers at the job site and as such their installation efficiency is limited by the time each layer or coating takes to set or dry. In addition, a quick drying exterior coating is needed so that it develops resistant to dirt pickup and washout by rain, snow, wind and the like so after its application. These problems associated with slow drying are exacerbated under certain environmental conditions, particularly cool and wet or humid conditions.

To reduce the cure time of the coatings, formulators have attempted to decrease the level of water in the coating formulation. However, this leads to coating formulations which are too viscous to apply.

Quick curing coatings are also needed for traffic paints so that they are not washed out by rain or marked by tire tread soon after application. Solvent-based paints dry quickly but pose serious safety, health and environmental problems. Conventional aqueous-based paints do not dry quickly enough, especially under cold and wet or humid conditions. Attempts to remedy this drying problem have lead to multiple step applications and storage stability problems.

For example, EP-A-0200,249 discloses applying an aqueous dispersion of polymer to the road and then contacting the composition with a second treatment containing a water soluble salt to cause the coating to dry rapidly and resist washout by a rain shower five minutes after application. EP-A-0,066,108 discloses an aqueous road marking composition in which the binder is a mixture of a pure acrylic resin, a carboxylated styrene/dibutyl fumarate copolymer and a polymeric, polyfunctional amine, such as polypropylenimine. The compositions are not storage stable beyond 48 hours after which more polyfunctional amine must be added to restore activity.

The present invention seeks to overcome the problems associated with the prior art aqueous compositions.

In particular, it is an object of the pres nt invention to solve the probl ms normally associated with conv ntional coatings by providing an aqu ous, xterior, quick-set coating which is storag stabl and asily ap-

plied and provides early washout resistance and dirt pick-up resistance.

It is also an object of th pr sent invention to provid a method for improving th arly washout resistance and dirt pick-up resistance of an aqueous, exterior, quick-set coating.

It is also a further object of th present inv ntion to provide a non-cementitious adh siv composition which is easily applied, provides arly cohesiv and adhesiv strength und r all curing conditions and l av s no waste.

It is a further object of the present invention to provide a method for improving the early cohesive and adhesive strength under all curing conditions of a non-cementitious adhesive.

According to a first aspect of the present invention there is provided an aqueous composition comprising (1) a film-forming latex polymer having anionic character; (2) an amine-containing polymer; and (3) a volatile base; and optionally (4) a water-soluble or water-dispersable multivalent metal ion.

According to a second aspect of the present invention there is provided an aqueous composition comprising: (a) a film-forming latex polymer having anionic character; (b) a water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups; and (c) a volatile base in an amount effective to raise the pH of the composition to a point high enough where essentially all of the amine functional groups are in a nonionic state.

According to a third aspect of the present invention there is provided a method of coating a substrate comprising applying a non-cementitious adhesive as defined in the first or second aspect of the present invention to a substrate, such as an exterior surface of a building or other outdoor structure, and applying a solid or foamed layer of protective material to said non-cementitious adhesive. According to a fourth aspect of the present invention there is provided a composite comprising: (a) a substrate; (b) an aqueous adhesive as defined above; and optionally (c) a layer of material adhered to said substrate.

Preferably the composition further comprises a water-soluble or water-dispersible multivalent metal.

Therefore according to a fifth aspect of the present invention there is provided an aqueous composition comprising (1) a film-forming latex polymer having anionic character; (2) an amine-containing polymer; (3) a volatile base; and (4) a multivalent metal ion.

According to a sixth aspect of the present invention there is provided an aqueous composition, in particular an aqueous exterior coating composition, comprising: (a) a film-forming latex polymer having anionic character; (b) a water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups; (c) a volatile base in an amount effective to raise the pH of the composition to a point high enough where essentially all of the amine functional groups are in a nonionic state; and (d) a water-soluble or water-dispersible multivalent metal.

According to a seventh aspect of the present invention there is provided a method for coating a substrate comprising applying a coating composition according to the first or second aspect of the present invention to a substrate.

Preferably the surface is an outdoor surface such as the side of a building or a road.

Preferably said water-soluble or water-dispersible polymer is formed from at least about 50% by weight monomer containing amine functional groups.

Preferably said water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups is an N-acryloxyalkyl-oxazolidine.

Preferably said volatile base is ammonia.

Preferably said water-soluble or water-dispersible multivalent metal is zinc.

This invention solves the problems encountered with conventional cementitious and non-cementitious adhesives by providing an aqueous, quick-set noncementitious composition which is easily applied, develops early cohesive and adhesive strength under all curing conditons and leaves no waste. The invention is particularly useful as an adhesive used in exterior insulating finishing systems. This invention also provides a method for improving the early adhesive and cohesive strength under all curing conditions of a non-cementitious adhesive.

In one preferred embodiment, the aqueous, quick-set, non-cementitious composition of this invention requires three components: (1) a film-forming latex polymer having anionic character; (2) an amine-containing polymer formed from at least 20% by weight monomer containing amine functional groups; and (3) a volatile base.

In another embodiment, the method for improving the early adhesive and cohesive strength of a non-cementitious adhesive under all curing conditions involves: (1) forming an non-cementitious adhesive containing: (a) a film-forming latex polymer having anionic character; (b) an amine-containing polymer; and (c) a volatile base; (2) applying the non-cementitious adhesive to the exterior surface of a building or other outdoor structure; and (3) applying a solid or foamed layer of protective material to the non-c mentitious adhesiv . Th refore an aqueous adhesive composition of the pres nt invention requires: (1) a film-forming latex polymer having anionic character; (2) an amine-containing polym r; and (3) a volatil bas .

The aqu ous adh sive composition of the present invention is "non-cementitious" which, as us d herein, means that the composition is compl t ly free of cement.

The aqueous adh sive compositi n of the present invention provides early adh siv and cohesiv strength und r all curing conditions.

As us d herein, the term "early" refers to the period when the aqueous composition is still wet.

"Cohesive strength," as used herein ref rs to the attractiv forc a material has for itself.

"Adhesive strength," as used herein refers to the attractive force a material has for a substrate and to the strength to bond surfaces together. The most stringent curing conditions for the aqueous adhesive composition of the present invention are cool and damp conditions.

The aqueous coating composition of the present invention also provides early washout resistance, dirt pick-up resistance and storage stability.

"Washout resistance," as used herein refers to the ability of a coating to resist becoming soft and blemished and washed away by rain, wind, snow and other harsh weather conditions and remaining an integral, unblemished coating.

"Dirt pick-up resistance," as used herein refers to the ability of a coating to resist soiling, particularly when the coating is still wet.

This invention also solves the problems encountered with conventional exterior coating compositions by providing an aqueous, exterior, quick-set coating composition having early washout resistance, dirt pick-up resistance and storage stability.

This invention also provides a method for improving the early washout resistance and dirt pick-up resistance of an aqueous, exterior, quick-set coating.

In one embodiment, the aqueous, exterior, quick-set coating composition of this invention requires four components: (1) a film-forming latex polymer having anionic character; (2) an amine-containing polymer formed from at least 20% by weight monomer containing amine functional groups; (3) a volatile base; and (4) a multivalent metal ion.

In another embodiment, the method of improving the early washout resistance and dirt pick-up resistance of an aqueous, exterior, quick-set coating involves: (1) forming an coating composition containing: (a) a film-forming latex polymer having anionic character; (b) an amine-containing polymer; (c) a volatile base; and (d) a multivalent metal ion; and (2) applying the coating to a substrate.

In another embodiment the invention provides an aqueous road or pavement marking paint. The paint can be used to mark lines or symbols on roads, parking lots, walkways and the like formed from various substances such as asphalt, bitumen, concrete and the like, with or without aggregate filler or top dressing. The paint dries quickly to develop early washout resistance and tire tread printing.

In another embodiment the invention provides an aqueous, exterior, quick-set coating useful as a base coat or top coat in multilayered exterior insulation and finishing systems ("EIFS").

The preferred aqueous coating composition of the present invention therefore requires: (1) a film-forming latex polymer having anionic character; (2) an amine-containing polymer; (3) a volatile base; and (4) a multivalent metal ion.

"Glass transition temperature," or "$T_g$," as used herein means the glass transition temperature of a polymer as calculated by the Fox equation [Bulletin of American Physics Society 1, 3, page 123 (1956)]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g(1)}} + \frac{w_2}{T_{g(2)}}$$

For a copolymer, $w_1$ and $w_2$ refer to the weight fraction of the two comonomers and $T_{g(1)}$ and $T_{g(2)}$ refer to the glass transition temperatures of the two corresponding homopolymers.

*FILM FORMING LATEX POLYMER*

The aqueous composition of the present invention requires a film-forming latex polymer having anionic character. "Latex" as used herein refers to a water-insoluble polymer which may be prepared by conventional polymerization techniques such as, for example, by emulsion polymerization. The latex polymer is formed from any monomer or mixture of monomers which yields a water-insoluble latex polymer which will form a film under the application conditions.

The $T_g$ of the latex polymer is limited only by the particular application for which the adhesive composition is to be used. For example, if an adhesive is to be applied outdoors in hot summer weather, then the composition of latex polymer may be selected to yield a $T_g$ greater than if the adhesive is to be applied outdoors in cold wint r w ather. Also, for example, if the coating is to b applied outdoors in hot summer weath r, then the composition of lat x polymer may be selected to yield a $T_g$ greater than if the coating is to b applied out-

doors in cold winter weather. Generally, the latex polymer has a $T_g$ from about -50°C to about 50°C. A coating containing a lat x polymer having a $T_g$ below -50°C is generally not useful since it is too soft and lack suffici nt strength to act as an adhesiv or it is too soft and sticky for coating applications.

A coating containing a latex polymer having a $T_g$ above 50°C is g nerally not useful since it is too hard to form a film even at higher than ambient temp ratures.

Polymers having a $T_g$ from about -15°C to about 10°C are preferred. Polym rs having a $T_g$ from about -10°C to about 5°C are most preferred.

The invention may also be practiced using polymers of more complex morphology, such as core-shell particles. These complex polymer morphologies usually display multiple $T_g$'s and may display a $T_g$ value outside the range of from about -50°C to about 50°C as one of its multiple $T_g$'s, however the average or effective $T_g$ of the polymer must be from about -50°C to about 50°C.

The anionic character of the film-forming latex polymer is obtained in any of several ways, the most common being the use of anionic surfactants or dispersants as the stabilizer during the emulsion polymerization or added to the emulsion after polymerization. Nonionic surfactants may also be present in the latex during or after polymerization of these anionically stabilized latexes.

Among the useful surfactants and dispersants are the salts of fatty rosin and naphthenic acids, condensation products of napthalene sulfonic acid and formaldehyde of low molecular weight, carboxylic polymers and copolymers of the appropriate hydrophile-lipophile balance, higher alkyl sulfates, such as sodium lauryl sulfate, alkyl aryl sulfonates, such as dodecylbenzene sulfonate, sodium or potassium isopropylbenzene sulfonates or isopropylnaphthalene sulfonates; sulfosuccinates, such as sodium dioctylsulfosuccinate alkali metal higher alkyl sulfosuccinates, *e.g.* sodium octyl sulfosuccinate, sodium N-methyl-N-palmitoyltaurate, sodium oleyl isethionate, alkali metal salts of alkylarylpolyethoxyethanol sulfates or sulfonates, *e.g.*. sodium t-octylphenoxypolyethoxyethyl sulfate having 1 to 5 oxyethylene units, and the various other anionic surfactants and dispersants well-known in the art.

Another type of latex polymer having anionic character is that which is obtained as a result of including in the polymer small amounts of acidic groups, which may be in the salt form, such as an alkali metal or ammonium salt.

Examples of such acidic groups are those derived from incorporated initiator fragments, maleic acid, vinyl sulfonic acid, crotonic acid, acrylic acid, methacrylic acid, itaconic acid, and the like.

A third useful type of latex polymer having anionic character is a latex polymer which includes a basic monomer which has been neutralized, such as for example acrylamide, methacrylamide and the like.

The latex polymer may have more than one type of anionic character.

The latex polymer having anionic character can be prepared by known procedures, which are published in texts on the subject such as <u>Emulsion Polymerization: Theory and Practice</u> by D. C. Blackley published by Wiley in 1975 and <u>Emulsion Polymerization</u> by F. A. Bovey *et al.* published by Interscience Publishers in 1965.

In general, the latex polymer is a polymer or copolymer prepared from monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acryate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, styrene, butadiene, ethylene, vinyl acetate, vinyl ester of "Versatic" acid (a tertiary monocarboxylic acid having $C_9$, $C_{10}$ and $C_{11}$ chain length, the vinyl ester is also known as "vinyl versatate"), vinyl chloride, vinyl pyridine, vinylidene chloride, acrylonitrile, chloroprene, acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid. Polymers and copolymers of $\alpha,\beta$-ethylenically unsaturated monomers and their esters, especially the acrylic and methacrylic esters, are preferred and are preferably prepared by processes given in "Emulsion Polymerization of Acrylic Monomers: May, 1966" published by the Rohm and Haas Company, Philadelphia, Pennsylvania, incorporated herein by reference.

*AMINE-CONTAINING POLYMER*

The aqueous composition of the present invention requires an amine-containing polymer which has been formed from at least 20% by weight of a monomer which contains amine functional groups. A polymer having at least 50% by weight of monomer containing amine functional groups is preferred. It is also preferable that the average molecular weight of the water-soluble or water-dispersible amine-containing polymer is from about 5,000 to about 100,000.

The examples of monomer containing amine functional groups include the following:

1. Aminoalkyl vinyl ethers or sulfides wherein the alkyl groups may be straight-chain or branched-chain type and have from two to three carbon atoms and wherein the nitrogen atom may be a primary, secondary, or t rtiary nitrogen atom (US-A-2,879,178).

In th latt r instance, one of the r maining hydrog n atoms may be substitut d by alkyl, hydroxyalkyl, or alkoxyalkyl groups, th alkyl compon nts of which may hav one to four carbon atoms, pr ferably one

carbon atom only.

Specific xamples include: β-aminoethyl vinyl ther; β-aminoethyl vinyl sulfid ; N-monom thyl-b-amino thyl vinyl ther or sulfide; N-monoethyl-β-aminoethyl vinyl ether or sulfid ; N-monobutyl-β-aminoethyl vinyl eth r or sulfide; and N-mono-methyl-3-aminopropyl vinyl ether or sulfide.

2. Acrylamide or acrylic esters, such as thos of the formula II:

$$H_2C{=}C(R)\overset{\displaystyle O}{\overset{\|}{C}}{-}(X)_n{-}A{-}NR^*R^0 \qquad (II)$$

wherein

R is H or $CH_3$;

n is 0 or 1;

X is O or N(H);

when n is zero, A is $O(CH2)_x$

wherein x is 2 to 3, or $(O\text{-alkylene})_y$ wherein $(O\text{-alkylene})_y$ is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene; and when n is 1, A is an alkylene group having two to 4 carbon atoms;

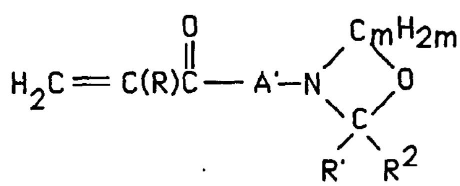
$R^*$ is H, methyl, or ethyl; and

$R^1$ is H, methyl, or ethyl; and

$R^0$ is H, phenyl, benzyl, methylbenzyl, cyclohexyl, or $(C_1\text{-}C_6)$ alkyl.

Examples of compounds of formula II include: dimethylaminoethylacrylate or methacrylate; β-aminoethyl acrylate or methacrylate; N-β-aminoethyl acrylamide or methacrylamide; N-(monomethylaminoethyl)-acrylamide or methacrylamide; N-(mono-n-butyl)-4-aminobutyl acrylate or methacrylate; methacryloxyethoxy ethylamine; and acryloxypropoxypropylamine.

3. N-acryloxyalkyl-oxazolidines and N-acryloxyalkyl tetrahydro-1,3-oxazines and the corresponding components in which the "alkyl" linkage is replaced by alkoxyalkyl and poly(alkoxy-alkyl), all of which are embraced by Formula III:



(III)

wherein

R is H or $CH_3$;

m is an integer having a value of 2 to 3;

R', when not directly joined to $R^2$, is selected from the group consisting of hydrogen, phenyl, benzyl, and $(C_1\text{-}C_{12})$ alkyl groups;

$R^2$, when not directly joined to R', is selected from the group consisting of hydrogen and $(C_1\text{-}C_4)$ alkyl groups;

R'and $R^2$, when directly joined together, form a 5- to 6-carbon ring with the attached carbon atom of the ring in the formula, *i.e.*, R'and R2 , when joined together, are selected from the group consisting of pentamethylene and tetramethylene; and

A' is $O(C_mH_{2m})$- or $(O\text{-alkylene})_n$ in which $(O\text{-alkylene})_n$is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene.

The compounds of Formula III can hydrolyze under various conditions to secondary amines. The hydrolysis produces products having the Formula IV:

$$H_2C{=}C(R)\overset{\overset{\large O}{\|}}{C}—A'—N(H)—(C_mH_{2m})—OH \qquad \text{(IV)}$$

The compounds of Formula III ar disclosed in US-A-3,037,006 and US-A-3,502,627 in the hands of a common assignee, and their corresponding foreign applications and patents and any of the monomeric compounds disclosed therein may be used in making the copolymers to be used in the composition of the present invention.

Examples of compounds of Formula III include:

oxazolidinylethyl methacrylate;
oxazolidinylethyl acrylate;
3-(γ-methacryl-oxypropyl)-tetrahydro-1,3-oxazine;
3-(β-methacryloxyethyl)-2,2-pentamethylene-oxazolidine;
3-β-methacryloxyethyl-2-methyl-2-propyloxazolidine;
N-2-(2-acryloxyethoxy)ethyl-oxazolidine;
N-2-(2-methacryloxyethoxy)ethyl-oxazolidine;
N-2-(2-methacryloxyethoxy)ethyl-5-methyl-oxazolidine;
N-2-(2-acryloxyethoxy)ethyl-5-methyl-oxazolidine;
3-[2-(2-methacryloxyethoxy)ethyl)]-2,2-penta-methylene-oxazolidine;
3-[2-(2-methacryloxyethoxy)ethyl)]-2,2-dimethyl-oxazolidine;
3-[2-(methacryloxyethoxy)ethyl]-2-phenyl-oxazolidine.

4. Polymers of monomers which readily generate amines by hydrolysis are useful as the amine-containing component or to generate the amine-containing component polymer of this binder composition. Examples of such monomers are acryloxy-ketimines and -aldimines, such as those of Formulas V and VI following:

$$H_2C{=}(CR)\text{-}COOA''N{=}Q \qquad \text{(V)}$$

$$H_2C = C(R)\text{-}CO\text{-}(D)_{n''-1} - (B)_{n'-1} - (A^o)_{n^o-1} - N = Q \qquad \text{(VI)}$$

wherein

R is H or $CH_3$;
Q is selected from the group consisting of

$$=C\begin{matrix} \diagup R^4 \\ \diagdown R^5 \end{matrix}\ , \qquad \underbrace{=C-(CHR^6)_x}_{\text{ring}}\ , \text{ and } =CHR^3\ ;$$

$R^6$ is H or it may be methyl in one $CHR^6$ unit;
$R^5$ is selected from the group consisting of $(C_1\text{-}C_{12})$-alkyl and cyclohexyl groups;
$R^4$ is selected from the group consisting of $(C_1\text{-}C_{12})$-alkyl and cyclohexyl;
$R^3$ is selected from the group consisting of phenyl, halophenyl, $(C_1\text{-}C_{12})$-alkyl, cyclohexyl, and $(C_1\text{-}C_4)$ alkoxyphenyl groups;
A" is a $(C_1\text{-}C_{12})$ alkylene group;
$A^o$, B and D are the same or different oxyalkylene groups having the formula $\text{-}OCH(R^7)\text{-}CH(R^7)\text{-}$wherein $R^7$ is H, $CH_3$, or $C_2H_5$;
x is an integer having a value of 4 to 5;
n° is an integer having a value of 1 to 200;
n' is an integer having a value of 1 to 200; and
n" is an integer having a value of 1 to 200, the sum of n -1, n'-1 and n"-1 having a value of 2 to 200.

Illustrative compounds of formulas V and VI are:

2-[4-(2,6-dimethylheptylidene)-amino]-ethylmethacrylate;
3-[2-(4-methylpentylidine)-amino]-propyl methacrylate;
β-(benzylideneamino)-ethyl methacrylate;
3- [2-(4-methylpentylidene)-amino]-ethylmethacrylate;
2-[4-(2,6-dimethylheptylidene)-amino]-ethylacrylate;
12-(cyclopentylid ne-amino)-dod cylm thacrylate;

N-(1,3-dimethylbutylidene)-2-(2-methacryloxyethoxy)-ethylamine;
N-(b nzylidene)-methacryloxyethoxyethylamine;
N-(1,3-dimethylbutylidene)-2-(2-acryloxyethoxy)-ethylamine;
N-(b nzyliden )-2-(2-acryloxyethoxy)ethylamine.

The compounds of Formulas V and VI hydrolyze in acid, neutral, r alkaline aqueous media to produce the corresponding primary amines or salts thereof in which the group -N = Q of the formulas becomes $-NH_2$ and O = Q. The compounds of Formulas V and VI are disclosed in US-A-3,037,969 and US-A-3,497,485, and any of the monomeric compounds therein disclosed may be used in the making of the copolymers to be used in the water-soluble polymer portion of the compositions of the present invention.

The preferred class of amine-containing polymers of this invention are water-soluble. By water-solubility is meant that the polymer is completely soluble either in free-base, neutral, or salt form. The solubility preferably exists at all pH's, especially in the range of about 4 to 10. A less preferred class of water-soluble amine-containing polymers are generally insoluble at high pH and soluble or partly soluble at acidic pH values, particularly in the pH range from about 4 to about 7.

By partly soluble is meant both the situation in which some of the polymer is soluble in water as well as that in which the entire polymer dissolves in the form of micelles or aggregates individual molecules, generally, highly water swollen aggregates. The latter are often called colloidal solutions.

It is preferred that most of the polymer be soluble at the acidic pH values.

The water-soluble amine-containing polymers of this invention include both the completely soluble and the partly soluble polymers as described immediately above.

A useful but still less preferred class of amine-containing polymers are those which are water-insoluble and, as will be noted below, have a molecular weight corresponding to the lower end of the range for the water-soluble counterparts.

These water-insoluble amine-containing polymers perform the same function as the water-soluble polymers. When these water-insoluble polymers are substituted for the water-soluble polymers, the early cohesive strength of the anionically stabilized latex polymer is improved; however, the improvement is usually not as great as that produced by the water-soluble polymers.

In general, the amine-containing polymers of at least 20% by weight of a monomer of categories 1, 2, 3, and 4, *supra,* may be obtained by solution polymerization in aqueous media, either neutral, alkaline, or acidic, depending upon the particular polymer sought. Generally, the polymerization is carried out in an aqueous medium containing a small amount of an acid, either organic or inorganic, such as acetic acid or hydrochloric acid. The amine-containing polymers include copolymers with up to 80% by weight one or more such as methyl acrylate, acrylamide, methacrylamide, and quaternary ammonium salts derived from the amine monomers, such as 2-methacryloxyethyl trimethyl ammonium chloride. Small amounts of relatively insoluble comonomers may also be used to obtain the water-soluble polymers.

The insoluble polymers may contain larger amounts of these comonomers. Such monomers include, as examples, acrylic acid esters with ($C_1$-$C_{18}$) alcohols and methacrylic acid esters with alcohols having one to 18 carbon atoms, especially ($C_1$-$C_4$) alkanols; styrene, vinyltoluene, vinyl acetate, vinyl chloride, vinylidene chloride, substituted styrenes, butadiene, substituted butadienes, ethylene; and the nitriles and amides of acrylic or of methacrylic acid. The particular comonomer or comonomers used in making a given amine-containing polymer depends upon the proportion of amine-containing monomer used in making the copolymer. Preferably, a comonomer with relatively high solubility in water is exclusively used to make the water-soluble polymers. The polymers are thus polymers or copolymers of cationic and, optionally, nonionic vinyl monomers. Examples of the cationic monomers are the amines, imines and quaternary ammonium salts; the other recited monomers are nonionic.

Thus, these water-soluble copolymers contain no acid groups other than trace amounts which may be present due to impurities in the monomers used or to small extent of hydrolysis during synthesis, storage or use.

The insoluble amine-containing polymers have a viscosity average molecular weight from about 5,000 to about 100,000, with the range of from about 15,000 to about 90,000 preferred.

The molecular weight of the water-soluble polymers may fall within a wide range; typically, the viscosity average molecular weight is from about 5,000 to about 300,000, with the range of from about 40,000 to about 100,000 preferred. The amount of the amine-containing polymer may range from about 0.1% to about 20% by weight of the total weight of anionic latex polymer and amine-containing polymer, the range from 0.5%, preferably 1%, to 8% being preferred.

Wat r-soluble amine-containing polymers include both th completely solubl and the partly solubl polymers. The term water-soluble amine-containing polymer describ s polym r that is completely soluble eith r in free-base, neutral, or salt form. Some polym rs are solubl at all pH's, while others are soluble ov r a rang

of pH for xampl from about 5 to 10. Other amine-containing polym rs are generally insoluble at high pH and soluble or partly soluble at acidic pH values, particularly in the pH range from about 5 to about 7. By partly solubl is meant both the situation in which some of the polym r is solubl in water as well as that in which the ntire polymer dissolves in the form of micelles or aggr gates of individual molecul s, g nerally, highly wat r swoll n aggregates. The latter are oft n called colloidal solutions. It is preferred that most of the polym r b solubl at the acidic pH values.

In general, the amine-containing polymers may be obtained by solution polymerization in aqueous media, either neutral, alkaline, or acidic, depending upon the particular polymer sought, as generally known in the art, for example as taught in US-A-4,119,600.

Generally, the polymerization is carried out in an aqueous medium containing a small amount of an acid, either organic or inorganic, such as acetic acid or hydrochloric acid. The amine-containing polymers include copolymers with up to 80% by weight one or more monoethylenically unsaturated monomers, such as methyl acrylate, acrylamide and methacrylamide.

Small amounts of relatively insoluble comonomers may also be used to obtain the water-soluble polymers. The insoluble polymers may contain larger amounts of these comonomers. Such monomers include, as examples, acrylic acid esters with ($C_1$-$C_{18}$) alcohols and methacrylic acid esters with alcohols having one to 18 carbon atoms, especially ($C_1$-$C_4$) alkanols; styrene, vinyltoluene, vinyl acetate, vinyl chloride, vinylidene chloride, substituted styrenes, butadiene, substituted butadienes, ethylene; and the nitriles and amides of acrylic or of methacrylic acid.

The particular comonomer or comonomers used in making a given amine-containing polymer depends upon the proportion of amine-containing monomer used in making the copolymer. The polymers are thus polymers or copolymers of cationic and, optionally, nonionic vinyl monomers. Examples of the cationic monomers are the amines and imines; the other recited monomers are nonionic. Thus, these water-soluble copolymers contain no acid groups other than trace amounts which may be present due to impurities in the monomers used or to small extent of hydrolysis during synthesis, storage or use.

*VOLATILE BASE*

The aqueous composition of this invention requires a volatile base. The type and amount of volatile base used must be sufficient to raise the pH of the composition to about the point where the amine functional groups of the amine-containing polymer are non-ionized (deprotonated), typically to at least pH 5, preferably from pH 7 to pH 9, to avoid interaction with the anionically stabilized latex polymer and other anionic components in the adhesive composition.

A starting point estimate of the amount of volatile base required to reach this point can be calculated from the number of equivalents of base needed to neutralize all of the acid groups in the latex (*i.e.* acid groups from: copolymerized carboxylic-bearing monomer; surfactant; or initiator) and the conjugate acid of the amine base.

If the amine is not sufficiently deprotonated, the emulsion will exhibit observeable signs of instability over time, such as viscosity increase and microscopically observeable "particle rafting," an early stage of aggregation/gellation. One equivalent of volatile base (based on latex acids and polyamine titers) is usually enough to yield a stable system although higher levels of volatile base (~3 to 4 equivalents) may be necessary for long term stability.

Higher amounts of volatile base can be used without departing from the spirit of the invention although the "quick dry" properties of the coating may be reduced. If the equipment used in the process of manufacture presents opportunities for loss of the volatile base by evaporation at any stage from when the volatile base is added until after the product is packaged in a sealed container, the amount of volatile amine loaded to the production equipment should be increased to offset the loss.

After application, the volatile base evaporates lowering the pH of the composition. When the pH of the composition falls to a point where the protonation of the amine functional group begins to occur, the amine functional group becomes cationic.

The quick dry is believed to be initiated by this conversion of the amine functional group to a cationic state in the presence of the anionically stabilized emulsion polymer, although the exact mechanism that produces the quick-dry property has not been established and we do not wish to bound by the theory of the exact mechanism.

Suitable volatile bases include but are not limited to ammonia, morpholine, alkyl amines, 2-dimethylaminoethanol, N-methylmorpholine, ethylenediamine, and mixtures thereof. Ammonia is preferred.

*MULTIVALENT METAL*

In the preferred embodiment, the aqueous quick-set, non-cementitious adhesive contains a water-solubl or wat r-disp rsibl multivalent metal in the form of a metal ion, salt, complex or oxide. Multival nt metal ions such as calcium, magnesium, zinc, barium, strontium, aluminum and the lik may be us d. Compl x s of multivalent metal ions, such as zinc h xammonia, zinc ammonium bicarbonate and the lik , and salts of multival nt metal ions with counterions, such as chloride, acetate, bicarbonate and the like, may be used. Zinc is the preferred multivalent metal.

The multivalent metal ion, salt, complex or oxide is useful at a level of from about 0.5% by weight to about 10% by weight, based on the weight of the latex polymer solids. A level of from about 1% by weight to about 7% by weight, based on the weight of the latex polymer solids, is preferred.

In addition, conventional additional components such as, for example those for adhesives and coatings - namely pigments, binders, vehicles, extenders, dispersants, surfactants, coalescents, wetting agents, rheology modifiers, thickeners, drying retarders, antifoaming agents, colorants, waxes, preservatives, heat stabilizers, solvents, anti-skinning agents, driers and the like - may be used in this invention.

Care must be exercised when selecting the type and amount of additives to avoid altering the pH of the composition to an extent that interferes with storage stability or buffering the pH to an extent that after application the pH does not fall sufficiently to initiate protonation of the polyamine.

For example an adhesive prepared using a polyamine with a relatively low pKa and too large an amount of calcium carbonate as filler, may display an unacceptably extended cure time.

The adhesive compositions of the invention typically have a solids content in the range of from about 10% by weight to about 75% by weight and a viscosity of from about 50,000 $mNsm^{-2}$ (centipoises) to about 300,000 $mNsm^{-2}$ (centipoises).

The aqueous, quick-set coating compositions of the present invention may contain fillers such as sand, calcium carbonate and the like. The coating may be applied by trowel, spraying and the like, typically in thickness of from about 0.08 cm (1/32 inch) to about 0.16 cm (1/8 inch).

The adhesive compositions of the present invention are useful in any type of construction adhesive application where early adhesive and cohesive strength is needed, such as for example, EIFS; cove base; floor tile including vinyl, ceramic, and wood; plywood and the like.

Therefore one method of the present invention is useful for improving the early cohesive strength of a non-cementitious adhesive. This method involves: (1) forming an non-cementitious adhesive containing: (a) film-forming latex polymer having anionic character; (b) an amine-containing polymer formed from at least 20% by weight monomer containing amine functional groups; and (c) a volatile base; (2) applying the non-cementitious adhesive to the exterior surface of a building or other outdoor structure; and (3) applying a solid or foamed layer of protective material to the non-cementitious adhesive.

The building and other structures may be formed from concrete, cement, brick, cinder block, wood, gypsum board, particle board and the like. The solid or foamed layer of protective material may be foamed polystyrene sheet and the like.

Another method of the present invention is useful for improving the early wash-out resistance and dirt pick-up resistance of an aqueous, quick-set coating.

This method involves: (1) forming an aqueous, quick-set coating containing: (a) a film-forming latex polymer having anionic character; (b) an amine-containing polymer formed from at least 20% by weight monomer containing amine functional groups; (c) a volatile base; and (d) a water-soluble or water-dispersible multivalent metal; and (2) applying the an aqueous, quick-set coating to a substrate.

The substrate may be formed from concrete, cement, brick, cinder block, wood, gypsum board, particle board, asphalt, bitumen and the like.

The present invention will now be described only by way of examples. For ease the Examples have been divided into two sections.

The FIRST SECTION concentrates on aqueous adhesive compositions.

The SECOND SECTION concentrates on aqueous coating compositions.

## FIRST SECTION

### EXAMPLE 1. PREPARATION OF ADHESIVE FORMULATIONS

The adhesives were prepared according to th following formulation by grinding tog th r th ingredi nts listed as grind ingredients in Tabl 1.1 and th n adding th remaining letdown ingr dients for each adhesiv formulation.

All quantities listed are in grams.

Table 1.1

| | Comparative Adhesive 1 | Adhesive 1 | Adhesive 2 |
|---|---|---|---|
| *Grind Ingredients* | | | |
| Anionically stabilized Latex Polymer (Rhoplex® AC-264 latex) (60% solids) | 330.7 | 330.7 | 330.7 |
| Ammonium hydroxide (28%) | 5 | 5 | 5 |
| Polyoxazolidinylethyl methacrylate (25% solids) | 0 | 4 | 4 |
| Zinc oxide | 0 | 0 | 100 |
| Calcium carbonate | 100 | 100 | 0 |
| Anionic dispersant (Tamol ® 850 dispersant) (30% total solids) | 2.5 | 2.5 | 2.5 |
| Potassium tripolyphosphate | 1.5 | 1.5 | 1.5 |
| Ethylene glycol | 2 | 2 | 2 |
| Texanol® coalescent (2,2,4-trimethyl-3-hydroxypentyl acetate) | 2 | 2 | 2 |
| Antifoaming agent (Nopco® NXZ antifoamer) | 4 | 4 | 4 |
| Clay filler | 15 | 15 | 15 |
| Marble dust | 400 | 400 | 400 |
| Sand #70 | 400 | 400 | 400 |
| *Letdown Ingredients* | | | |
| Water | 20 | 20 | 20 |
| Hydroxyethyl cellulose (Natrasol® HR thickener) | 0.3 | 0.3 | 0.3 |

## EXAMPLE 2. SET TIME

The adhesive formulations were tested to determine how long they took to completely set. The test specimens were prepared by casting each adhesive formulation on Teflon®-coated glass at a thickness of from about 0.079 cm (1/32 inch) to about 0.16 cm (1/16 inch).

Testing was done at a temperature of 22.2°C (72°F) and relative humidity of 32.8%. A Gardner Set Time Recorder was then placed on each freshly made test specimen. The probe on the recorder moves at one revolution per hour through or on top of the adhesive. Set time is reported in minutes and was established when the probe completely moved on the surface of the adhesive without making any trace mark on the surface.

Short set times are desirable because they indicate that the adhesive builds early cohesive and adhesive strength.

The results are reported in Table 2.1.

Table 2.1

| Adhesive | Set Time (minutes) |
|---|---|
| Comparative 1 | 85 |
| 1 | 60 |
| 2 | 35 |

The set time d cr ased by 25 minutes for th adhesive formulation made according to th invention (Adh sive 1).

The set time decreased by a total of 50 minut s for the adh sive formulation made according to the invention which optionally contained multivalent metal (Adhesiv 2 -- contained zinc oxide).

**EXAMPLE 3. TENSILE STREN TH TESTING**

The adhesive formulations w r tested for early tensile bond strength und r a vari ty of curing conditions to demonstrate that the aqueous adhesive compositions of the invention showed improved properties under all curing conditions. In a pre-equilibration chamber, samples were prepared by using a two-part epoxy to glue circular pieces of expanded polystyrene foam (2.54 cm (1 inch) thick) to a wood disk (5.7 cm (2.25 inch) diameter; 1.27 cm (0.5 inch) thick). In a like manner, plywood was also glued to a second wood disk.

A layer of each adhesive formulation was applied onto the plywood surface of the second wood disk using a spatula and then polystyrene side of the first wood disk was firmly pressed against the layer of adhesive. Each sample was then cured. Before testing, all samples were equilibrated to test conditions. The sample was then placed in the jaws of an Instron testing machine with the sample being pulled apart at an angle perpendicular to the layer of adhesive. All samples were tested at a crosshead speed of 1.27 cm(0.5 inches)/minute. Tensile strength was reported in x 14.3 kg/cm$^2$ - which is equivalent to x 1 pound per square inch (based on the calculation that 1 lb/in$^2$ is equivalent to 0.7 kg/cm$^2$)- as the ratio of the load at break from the Instron (pounds) to the surface area of the test specimen (square inches). The results are reported in Table 3.1. High tensile strengths at break are desirable. In addition, substrate failure (polystyrene) types are more desirable than adhesive failure types.

Table 3.1

| | Comparative | Adhesive Adhesive 1 | Adhesive 1 | 2 |
|---|---|---|---|---|
| Tensile strength* at break (pounds/square inch) | 20.1 | 25.3 | 34.4 | |
| *NOTES:* *Cured at ambient conditions for 4 hours* *Tested at 75°F **and 50% relative humidity -- warm* *Thickness of adhesive = 1/32 inch**** | | | | |
| Tensile strength* at break (pounds/square inch) | 3.4 | 7.5 | 13.6 | |
| *NOTES:* *Cured at ambient conditions for 3 hours* *Tested at 75°F **and 50% relative humidity -- warm* *Thickness of adhesive = 1/8 inch***** | | | | |
| Tensile strength* at break (pounds/square inch) | 16.6 | 19.0 | 29.5 | |
| Failure type | 100% adhesive | 90% adhesive failure substrate failure | 100% substrate failure/10% | failure |
| *NOTES:* *Cured at ambient conditions for 2 hours* *Tested at 75°F **and 50% relative humidity -- warm* *Reported as average of 5 measurements* *Thickness of adhesive = 1/16 inch****** | | | | |
| Tensile strength *at break (pounds/square inch) | 21.6 | 31.4 | 34.9 | |
| Failure type | 70% adhesive | 100% substrate failure/30% substrate failure | 100% substrate failure | failure |

*NOTES:*
*Cured at 82°F ******and 94.5% relative humidity for 5 hours -- warm and very humid*
*Tested at 75°F **and 50% relative humidity -- warm*
*Reported as average of 5 measurements*
*Thickness of adhesive = 1/16 inch*
*x 14.3 kg/cm$^2$ - which is equivalent to x 1 pound per square inch (based on the calculation that 1 lb/in$^2$ is equivalent to 0.7 kg/cm$^2$)
** equivalent to 24°C - ***equivalent to 0.08 cm - ****equivalent to 0.32 cm - *****equivalent to 0.16 cm - ******equivalent to 28°C

The tensile strength increased at both thicknesses for the adhesive formulation made according to the inv ntion (Adh sive 1) as compared to the th adhesiv which did not contain an amin -containing polym r (Comparative Adhesive 1). The tensile strength increased even more at both thicknesses for the adhesiv formulation made according to the invention which optionally contained multivalent metal (Adhesive 2 -- contain d

zinc oxid ).

Th tensile str ngth increased for the adhesive formulation made according to the invention (Adhesive 1) as compared to the th adhesiv which did not contain an amin -containing polymer (Comparativ Adhesive 1) under warm conditions and very humid conditions. The t nsil strength increas d even more for the adh - siv formulation made according to th invention which optionally contained multivalent metal (Adh sive 2 -- contain d zinc oxid ) under warm conditions and under wet and very humid conditions. Under warm conditions, the adhesive which optionally contained the zinc oxide experienced a desirable 100% substrate failure (Adhesive 2) and the comparative adhesive experienced an undesirable 100% adhesive failure. Under very humid curing conditions, Adhesive 1 and Adhesive 2 both experienced a desirable 100% substrate failure.

## EXAMPLE 4. SHEAR STRENGTH TESTING

The adhesive formulations were tested for early shear strength under a variety of curing conditions to demonstrate that the aqueous adhesive compositions of the invention showed improved properties under all curing conditions. In a pre-equilibration chamber, samples were prepared by using a two-part epoxy to glue rectangular pieces of expanded polystyrene foam (2.54 cm (1 inch) thick) to a wood piece (7.62 cm (3 inches) by 5.08 cm (2 inches)).

In a like manner, plywood or cementitious board was cut into 7.62 cm by 5.08 cm (3 inch-by-2 inch) pieces.

A layer of each adhesive formulation (0.16 cm - 0.08 cm (1/32-1/16 inch thickness)) was applied onto the plywood or cementitious board using a spatula and then polystyrene side of the wood piece was firmly pressed against the layer of adhesive. Each sample was then cured at room temperature. Before testing, all samples were equilibrated to test conditions. The sample was then placed in the jaws of a Tinius Olsen Stress Tester with the sample being pulled apart at an angle 180° to the layer of adhesive. All samples were tested at a crosshead speed of 1.27 cm (0.5 inches)/minute. Shear strength was reported in pounds per square inch as the ratio of the load at break from the Stress Tester (pounds) to the surface area of the test specimen (square inches). The results are reported in Table 4.1. High shear strengths at break are desirable. In addition, substrate failure types are more desirable than adhesive failure types.

Table 4.1

| | Comparative Adhesive 1 | Adhesive 1 | Adhesive 2 |
|---|---|---|---|
| ***Plywood Substrate*** | | | |
| Shear strength *at break (pounds/square inch) | 7.5 | 9.7 | 11.7 |
| Failure type | 100% adhesive failure | 90% adhesive failure/10% substrate failure | 90% adhesive failure/10% substrate failure |

NOTES:
*Cured at 75°F *and 50% relative humidity for 3 hours -- warm*
*Tested at 75°F* and 50% relative humidity -- warm*
*Reported as average of 2 measurements*

| | Comparative Adhesive 1 | Adhesive 1 | Adhesive 2 |
|---|---|---|---|
| ***Cementitious Substrate*** | | | |
| Shear strength* at break (pounds/square inch) | 9.0 | 13.1 | 16.2 |
| Failure type | 90% adhesive failure/10% substrate failure | 80% adhesive failure/20% substrate failure | 20% adhesive failure/80% substrate failure |

NOTES:
*Cured at 75°F *and 50% relative humidity for 3 hours -- warm*
*Tested at 75°F *and 50% relative humidity -- warm*
*Reported as average of 2 measurements*
*x 14.3 kg/cm² - which is equivalent to x 1 pound per square inch (based on the calculation that 1 lb/in² is equivalent to 0.7 kg/cm²)
** equivalent to 24°C

The shear strength increased on both types of substrates for the adhesive formulation made according to the invention (Adhesive 1) as compared to the adhesive which did not contain an amine-containing polymer (Comparative Adhesive 1) under warm conditions. The shear strength increased on both types of substrates even more for the adhesive formulation made according to the invention which optionally contained multivalent metal (Adhesive 2 -- contained zinc oxide) under warm conditions.

## SECOND SECTION

### EXAMPLE 1. PREPARATION OF COATING FORMULATIONS

The coatings wer prepared according to the following formulation by grinding together th ingredients listed as grind ingredients in Table 1.1 and th n adding the remaining letdown ingredients for each coating formulation.

Table 1.1

| | Comparative 1 | Comparative 2 | Comparative 3 | Comparative 4 | 1 | 2 |
|---|---|---|---|---|---|---|
| *Grind Ingredients* | | | | | | |
| Anionically stabilized Latex Polymer (Rhoplex® AC-264 latex ) (60% solids) | 330.7 | 330.7 | 263.6 | 263.6 | 330.7 | 263.6 |
| Ammonium hydroxide (28%) | 5 | 5 | to pH 10 | to pH 10 | 5 | to pH 10 |
| Polyoxazolidinylethyl methacrylate (25% solids) | 0 | 2.4 | 0 | 1.9 | 2.4 | 3.2 |
| Zinc oxide | 0 | 0 | 0 | 0 | 100 | 0 |
| Zinc ammonium bicarbonate (8.4%) | 0 | 0 | 0 | 0 | 0 | 3.2 |
| Calcium carbonate | 100 | 100 | 0 | 0 | 0 | 0 |
| Anionic dispersant (Tamol ® 850 dispersant) (30% total solids) | 2.5 | 2.5 | 0 | 0 | 2.5 | 0 |
| Potassium tripolyphosphate | 1.5 | 1.5 | 0 | 0 | 1.5 | 0 |
| Ethylene glycol | 2 | 2 | 1 | 1 | 2 | 1 |
| Texanol® coalescent (2,2,4-trimethyl-3-hydroxypentyl acetate) | 2 | 2 | 6.5 | 6.5 | 2 | 6.5 |
| Antifoaming agent (Nopco® NXZ antifoamer) | 5 | 5 | 2 | 2 | 5 | 2 |
| Clay filler | 15 | 15 | 0 | 0 | 15 | 0 |
| Marble dust | 400 | 400 | 0 | 0 | 400 | 0 |
| Sand #70 | 400 | 400 | 0 | 0 | 400 | 0 |
| Sand #125 | 0 | 0 | 905.3 | 905.3 | 0 | 905.3 |
| Silica flour #120 | 0 | 0 | 250.0 | 250.0 | 0 | 250.0 |
| Mica (Alzibronz® 88) | 0 | 0 | 30.0 | 30.0 | 0 | 30.0 |
| Polyester fiber (1/4 inch) | 0 | 0 | 2.0 | 2.0 | 0 | 2.0 |
| *Letdown Ingredients* | | | | | | |
| Water | 20 | 20 | 209.5 | 209.5 | 20 | 209.5 |
| Hydroxyethyl cellulose (Natrasol® HR thickener) | 0.3 | 0.3 | 0.35 | 0.35 | 0.3 | 0.35 |

### EXAMPLE 2. SET TIME

The coating formulations were tested to determine how long they took to completely set. The test specimens were prepared by casting each coating formulation on Teflon®-coated glass at a thickness of from about 0.08 cm (1/32 inch) to about 0.15 cm (1/16 inch).

Testing was done at a temperature of 22°C (72°F) and relative humidity of 32.8%. A Gardner Set Time Recorder was then placed on each freshly made test specimen. The probe on the recorder moves at one revolution per hour through or on top of the coating. Set time is reported in minutes and was established when the probe complet ly moved on the surface of the adh sive without making any trac mark on the surfac . Short s t times are desirable because they indicate that the adhesive builds early cohesive and adhesive strength.

The results are reported in Table 2.1.

Table 2.1

| Test Specimen | Test M thod | S t Time (minut s) |
|---|---|---|
| Comparativ 1 | partial | 60 |
| Comparativ 1 | complete | 85 |
| | | |
| Comparative 2 | partial | 43 |
| Comparative 2 | complete | 60 |
| | | |
| 1 | partial | 18 |
| 1 | complete | 35 |

The set time test demonstrated that the coating of the invention (Coating 1) gave a shorter partial and complete set time as compared to the coating containing no amine-containing polymer and no multivalent metal (Comparative 1) and as compared to the coating containing amine-containing polymer but no multivalent metal (Comparative 2).

**EXAMPLE 3. EARLY WASHOUT RESISTANCE**

The coating formulations were tested for early washout resistance. The test specimens were prepared by casting each coating formulation at a thickness of 0.0625 cm (1/16 inch) on an expanded polystyrene board. The test specimens were then cured at the following conditions:

| Condition | Temperature (°C) | Relative Humidity | Duration (hours) |
|---|---|---|---|
| A | 10 | 80% | 5 |
| B | 24 | 70% | 2 |
| C | 24 | 50% | 2 |
| D | 24 | 50% | 3 |
| E | 24 | 50% | 4 |
| F | 4 | 50-60% | 3 |
| G | 4 | 50-60% | 4 |
| H | 4 | 50-60% | 5 |
| I | 4 | 50-60% | 6 |

The test specimens were then held at a 45° under a stream of cold running water at a flow rate of 818 litres/hour (180 gallons/hour). Failure was noted at the time when erosion of the coating was first seen. The higher the time to washout, the better the washout resistance. The results are shown in Table 3.1.

Table 3.1

| Test Sp cimen Condition | Wash-out Resistance | |
|---|---|---|
| Comparative 3 | A | complete washout in <2 hours |
| Comparative 3 | B | surfac washout at 5 hours |
| Comparative 3 | C | complete washout immediately |
| Comparative 3 | D | complete washout immediately |
| Comparative 3 | E | complete washout in 2 minutes |
| Comparative 3 | F | complete washout immediately |
| Comparative 3 | G | complete washout in 1 minute |
| Comparative 3 | H | complete washout in 3 minutes |
| Comparative 3 | I | complete washout in 5 minutes |
| Comparative 4 | C | complete washout immediately |
| Comparative 4 | D | complete washout in 2 minutes |
| Comparative 4 | E | complete washout in 4 minutes |
| Comparative 4 | F | complete washout immediately |
| Comparative 4 | G | complete washout in 2 minutes |
| Comparative 4 | H | complete washout in 10 minutes |
| Comparative 4 | I | complete washout in 14 minutes |
| 1 | A | only one soft spot in >5 hours |
| 1 | B | no washout or soft spots in 7 hours |
| 1 | C | complete washout in 5 minutes |
| 1 | D | complete washout in 16 minutes |
| 1 | E | complete washout in 30 minutes |
| 1 | F | complete washout in 1 minute |
| 1 | G | complete washout in 6 minutes |
| 1 | H | complete washout in 18 minutes |
| 1 | I | complete washout in 30 minutes |
| 2 | C | complete washout in 5 minutes |
| 2 | D | complete washout in 17 minutes |
| 2 | E | complete washout in 30 minutes |
| 2 | F | complete washout in 2 minute |
| 2 | G | complete washout in 4 minutes |
| 2 | H | complete washout in 15 minutes |
| 2 | I | complet washout in 30 minut s |

Th early washout resistanc test demonstrated that the coatings of the invention (Coatings 1 and 2) gav bett r washout r sistance as compared to the coating containing no amine-containing polymer and no multivalent metal (Comparative 3) and as compared to the coating containing amine-containing polymer but no multivalent m tal (Comparative 4) under all curing conditions.

**EXAMPLE 4. DIRT PICK-UP RESISTANCE**

The coating formulations were tested for dirt pick-up resistance. The test specimens were prepared by casting each coating formulation on a 8.25 cm (3 1/4 inch) by 43 cm (17 inch) scrub test panel at a thickness of 1/16 inch according to ASTM D-2486. The test specimens were then cured for 24 hours under ambient conditions.

***Test Method 1***

Brown ferric oxide was mechanically mixed with deionized water until smooth to form a slurry. The ferric oxide slurry was brushed on one half of each panel and then dried for 3 hours at room temperature. Each panel was then washed thoroughly under running tap water wiping with a cheese cloth to remove all the excess ferric oxide. Each panel was dried for an additional 2 hours.

Each panel were then tested using a Menotar C231 Colorimeter reading the reflectance of the stained half and the unstained half. The degree of dirt pick-up is reported as the % reflectance retained:

$$\%\ \text{reflectance retained} = \frac{\text{reflectance of stained portion}}{\text{reflectance of unstained portion}} \times 100\%$$

The higher the % reflectance retained, the better the dirt pick-up resistance. The results are reported in Table 4.1.

***Test Method 2***

Approximately 1-2 grams ASTM standard artificial soil was rolled over a cured panel using a SCUZZOMETER soiling tester. 1-2 grams standard soil was also sprinkled evenly on the roller and its track on the test panel.

The soiling tester was then run for the same cycles for each panel (20 cycles -- designated as Test Method 2A or 100 cycles -- designated as Test Method 2B). During the cycling, the standard soil was occasionally brushed back into the roller track. At the end of the cycling, the panel was wiped firm with a clean tissue to remove any loose soil.

Each panel were then tested using a Menotar C231 Colorimeter reading the reflectance of the stained half and the unstained half. The degree of dirt pick-up is reported as the % reflectance retained:

$$\%\ \text{reflectance retained} = \frac{\text{reflectance of stained portion}}{\text{reflectance of unstained portion}} \times 100\%$$

The higher the % reflectance retained, the better the dirt pick-up resistance. The results are reported in Table 4.1.

Tabl 4.1

| T st Specimen Test M thod | % Refl ctance R tained | |
|---|---|---|
| Comparative 1 | 1 | 49.1 |
| Comparative 1 | 2A | 80.4 |
| Comparative 1 | 2B | 83.1 |
| | | |
| Comparative 2 | 1 | 52.1 |
| Comparative 2 | 2A | 86.8 |
| Comparative 2 | 2B | 84.5 |
| | | |
| 1 | 1 | 54.1 |
| 1 | 2A | 89.4 |
| 1 | 2B | 89.6 |

The dirt pick-up resistance test demonstrated that the coating of the invention (Coating 1) gave better resistance as measured by all of the test methods as compared to the coating containing no amine-containing polymer and no multivalent metal (Comparative 1) and as compared to the coating containing multivalent metal but no amine-containing polymer (Comparative 2).

## Claims

1. An aqueous composition comprising
   (1) a film-forming latex polymer having anionic character;
   (2) an amine-containing polymer; and
   (3) a volatile base; and optionally
   (4) a multivalent metal ion.

2. A composition according to claim 1 comprising:
   (a) a film-forming latex polymer having anionic character;
   (b) a water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups; and
   (c) a volatile base in an amount effective to raise the pH of the composition to a point high enough where essentially all of the amine functional groups are in a nonionic state; and optionally
   (d) a water-soluble or water-dispersible multivalent metal.

3. A composition according to claim 1 or claim 2 comprising a water-soluble or water-dispersible multivalent metal.

4. A composition according to any one of the preceding claims wherein said water-soluble or water-dispersible polymer is formed from at least about 50% by weight monomer containing amine functional groups.

5. A composition according to any one of the preceding claims wherein said water-soluble or water-dispersible polymer formed from at least about 20% by weight monomer containing amine functional groups is an N-acryloxyalkyl-oxazolidine.

6. A composition according to any one of the preceding claims wherein said volatile base is ammonia.

7. A composition according to claim 3 or any claim d pendent ther on wher in the multivalent m tal is zinc.

**8.** A method for coating a substrat comprising applying a composition as d fined in any one of th preceding claims to th substrate, pr ferably wherein the substrate is an outdoor surfac such as a road or th sid of a building.

**9.** A method of coating a substrate comprising applying a non-cem ntitious adhesive as defined in any one of claims 1 to 7 to a substrate, such as an ext rior surface of a building or oth r outdoor structure, and applying a solid or foamed layer of protective material to said non-cementitious adhesive.

**10.** A composite comprising:
(a) a substrate;
(b) a composition as defined in any one of claims 1 to 7; and optionally
(c) a layer of material adhered to said substrate.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 93 30 7857

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.5) |
|---|---|---|---|
| X | EP-A-0 409 459 (ROHM AND HAAS COMP)<br>* claims 1-6; examples *<br>----- | 1 | C08L101/08<br>C08L101/02<br>E04F13/08<br>B05D5/00<br>//(C08L101/08, 39:00),<br>(C08L101/02, 33:06) |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.5) |
| | | | C09D<br>C09J<br>E04F |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 10 February 1994 | Schueler, D |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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